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The Rhynie Chert, Scotland, and the Search for Life on Mars

Louisa J. Preston* and Matthew J. Genge

Abstract

Knowledge of ancient terrestrial hydrothermal systems—how they preserve biological information and how this information can be detected—is important in unraveling the history of life on Earth and, perhaps, that of extinct life on Mars. The Rhynie Chert in Scotland was originally deposited as siliceous sinter from Early Devonian hot springs and contains exceptionally well-preserved fossils of some of the earliest plants and animals to colonize the land. The aim of this study was to identify biomolecules within the samples through Fourier transform infrared (FTIR) spectroscopy and aid current techniques in identification of ancient hot spring deposits and their biological components on Mars.

Floral and faunal fossils within the Rhynie Chert are commonly known; but new, FTIR spectroscopic analyses of these fossils has allowed for identification of biomolecules such as aliphatic hydrocarbons and OH molecules that are potentially derived from the fossilized biota and their environment. Gas chromatograph–mass spectrometer (GCMS) data were used to identify *n*-alkanes; however, this alone cannot be related to the samples' biota. Silicified microfossils are more resistant to weathering or dissolution, which renders them more readily preservable over time. This is of particular interest in astropaleontological research, considering the similarities in the early evolution of Mars and Earth. Key Words: Biomarkers—Fossilization—Hot spring—IR spectroscopy—Mars. *Astrobiology* 10, 549–560.

1. Introduction

STUDIES OF EXTREME ENVIRONMENTS known to harbor life on Earth have allowed for analogies to be made with regard to conditions on other planetary bodies in the quest to discover life beyond the confines of Earth. Progress in this search is continuing to be made through the studies of chemical and fossil signatures of life and through analyses of environments that are best suited to nurture and preserve them. Hydrothermal systems are such an environment due to the heat, nutrients, and protection they afford varied ecosystems. Hydrothermal systems formed either by magmatic or impact-related processes are widespread on Earth and have occurred, and may still occur, on Mars.

The purpose of the present investigation was to study the Rhynie Chert in Scotland, an ancient hydrothermal system with a known, well-preserved biota. Our intent was to facilitate identification of similar deposits on Mars and ascertain the potential for identification of fossilized biomolecules via Fourier transform infrared (FTIR) spectroscopy and gas chromatography–mass spectrometry techniques suitable for planetary surface exploration.

1.1. Geological setting of the Rhynie Chert

The Rhynie Chert Site of Special Scientific Interest represents the surface manifestation of a ~396 Ma subaerial hot spring system (Rice *et al.*, 1995) and is one of the earliest known silicified terrestrial ecosystems with a well-preserved biota. The cherts are found near Aberdeen, Scotland (Fig. 1a), in a succession of Early Devonian sedimentary and volcanic rocks (Rice *et al.*, 2002). Hot spring activity produced silica sinters that, over millions of years, have become cherts and contain the preserved remains of vascular land plants (Kidston and Lang, 1917, 1920a, 1920b, 1921a, 1921b; Remy and Remy, 1980; Hass, 1991), lichens (Taylor *et al.*, 1995, 1997), fungi (Hass *et al.*, 1994), algae (Edwards and Lyon, 1983), terrestrial arachnids (Dunlop, 1994), an insect (springtail) (Whalley and Jarzembowski, 1981), and freshwater crustaceans (Scourfield, 1926).

By the Early Devonian, the Iapetus Ocean had closed and was replaced by a transtensional regime with sinistral shearing and major igneous activity in northern Britain (Patrick and Polya, 1993; Stewart *et al.*, 1999; Treagus *et al.*, 1999). Essential features required to establish a hot spring

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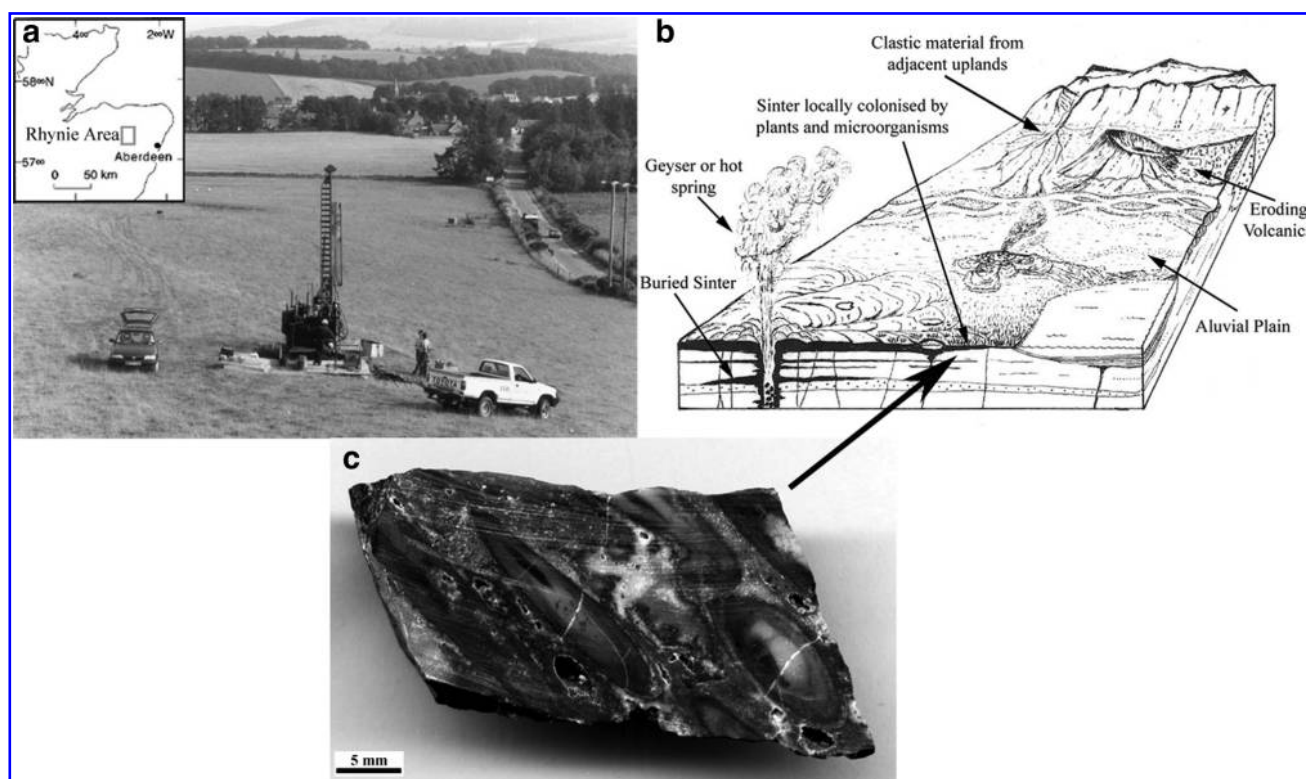


FIG. 1. (a) Photograph of drilling in the Rhynie Chert Site of Special Scientific Interest at Rhynie in 1997 (Trewin, 2004) with inset map of Scotland showing the location of Rhynie (adapted from Rice *et al.*, 2002). (b) Reconstruction of the Rhynie environment 396 million years ago (adapted from Trewin, 2001). (c) A sample of the Rhynie Chert from the private collection of Dr. Anton Kearsley. Arrow shows where in the original environment this sample is expected to have originated.

system, such as the system at Rhynie, are open structures and sources of heat and water, which were abundant in northern Britain at this time and allowed hot spring activity to be widespread (Nicholson, 1989). Rhynie lies on a major northeast-trending fault; and local igneous activity, probably related to large heat flow generated by emplacement of large granitic intrusions at shallow depth in the crust, may have provided the energy to sustain the hot springs. The preservation of the Rhynie succession was due to hot spring activity that coincided with active sedimentation in a subsiding basin (Fig. 1b). The Rhynie area itself was a small half graben that contained an alluvial plain and ephemeral lakes, with a semi-arid climate, and was affected by volcanic activity (Trewin and Rice, 1992).

The cherts found here are the first recorded surface manifestations of hydrothermal activity. They appear late in the basin history and are hosted by the lacustrine and flood plain deposits of the Dryden Flags Formation (Rice *et al.*, 2002). More than 50 chert beds are associated with carbonaceous sandstones and lacustrine shales in the Rhynie Chert Unit (~35 m thickness in the Rhynie area).

1.2. Biota of the Rhynie Chert

More than 10 fossiliferous beds have been identified in the Rhynie Chert deposit (Trewin and Rice, 1992) with the biota preserved as siliceous permineralizations. The final preservation states of permineralized fossils depend upon the state of decay reached when the organism or plant became infil-

trated by the fossilizing medium. Plant remains were discovered in the Rhynie Chert by Mackie (1913) with subsequent detailed accounts by Kidston and Lang (1917, 1920a, 1920b, 1921a, 1921b). Kidston and Lang (1921b) provided the first report of the microbial components in the Rhynie ecosystem in the form of fungal hyphae, thick-walled resting spores, and clusters of cells they interpreted as bacteria. They also recognized the role that the Rhynie Chert fungi played in nutrient cycling, that is, as biotrophs they interacted with the macroplants, and that some fungi may have formed symbiotic associations with one or more of the land plants. A large number of microbial interactions have been documented from the Rhynie Chert, but many are yet to be understood.

The Devonian was an exceptional time for the evolution of plants, and the fossilized specimens of the Rhynie Chert provide a unique insight into early terrestrial ecosystems and their components. Minute details of the plants have been preserved, including cell detail (Kidston and Lang, 1917, 1920a, 1920b, 1921a, 1921b), fragile root-like rhizoids, spores and reproductive structures (Lyon, 1957; Remy and Hass, 1996), vascular systems, gametophyte generations (Remy and Remy, 1980; Remy *et al.*, 1993), and even seasonal growth. There are seven genera of terrestrial macroplants described from the Rhynie Chert. *Rhynia* and *Aglaophyton* are the most abundant.

Within the Rhynie Chert there are a variety of examples of fungi that occur as saprophytes (organisms that grow on, and derive nourishment from, dead and decaying organic

matter) of plants and animals and as parasites (organisms that obtain nourishment from other living organisms or dead organic matter, or both) of macroplants, algae, and other fungi (Taylor *et al.*, 2004). Some of these fungi were shown by Kidston and Lang (1921b) as thick-walled resting fungal spores (chlamydospores) with smaller spores inside of intrusive fungi.

Kidston and Lang (1921b) described bacteria in the matrix that were associated with some plant material; further studies identified additional colonies and clusters of bacterial cells that appear similar to cyanobacteria (Croft and George, 1959). A new filamentous cyanobacterium described by Krings *et al.* (2007), species *Croftalania venusta* M. Krings, Kerp, Hass, T.N. Taylor et Dotzler, is associated with the formation of microbial mats.

Chlorophytes are a division of eukaryotic algae that is comprised of green algae that contain chlorophyll *a* and *b* in chloroplasts, and embryophytes with accessory pigments of beta carotene and xanthophylls, and a unique stellate structure (Mattox and Stewart, 1984; Sluiman, 1985; Bremer *et al.*, 1987; Kenrick and Crane, 1997). Chlorophytes are designated as nonvascular plants and are typically found in freshwater environments. They are among the oldest known fossils and have been recorded in the Precambrian Ediacara Fauna with a number of unicellular and filamentous types of chlorophytes described from the Rhynie Chert.

1.3. Mineralogy and preservation

Biomolecules and other evidence for past life are preserved such that they can be accurately identified. The Rhynie Chert is an excellent example of this. It was initially deposited as highly porous amorphous silica comparable to modern-day silica sinter hot spring deposits. The ecosystem was cemented by silica and transformed to chert in the shallow subsurface of the hydrothermal system (Trewin, 1996). The Rhynie Chert is relatively unaltered and lacks physical evidence of geyser activity. Parallel-laminated cherts indicative of stromatolitic sinter apron deposits form a very minor part. Trewin and Wilson (2004) suggested that the Rhynie chert sequence represents deposition in a low-relief area, probably the distal, cooler parts of a hydrothermal discharge apron. The hydrothermally altered nature of the sediments that host the nearby Windyfield Chert, and the presence of a chert block that represents a geyser vent rim, indicate that deposition occurred in an area proximal to hydrothermal activity with a flux of upward-migrating hot fluids (Fayers and Trewin, 2004).

The Rhynie chert biota has been preserved via rapid silicification of organic material by thermal fluids that issue from a hot spring; however, the quality of preservation of the Rhynie biota is variable (Trewin, 1996). Experiments have shown that the silicification of plant material is a permeation and void-filling process (or permineralization) rather than the direct replacement of cell walls (or petrification), where the organic structure acts as a template for silica deposition. The three main potential processes for preservation are surface flooding, a hot spring pool, and surface permeation (Trewin, 1996). Plant and arthropod material are found silicified in all stages of decay. Transported material and degraded plant litter showing breakdown of tissue structure and infestation of fungi can be perfectly silicified, but the

details of plant structure are best preserved when the growing plants were engulfed in the Si-rich hot spring waters.

2. Materials and Methods

The samples of Rhynie Chert were obtained from teaching materials owned by Dr. Anton Kearsley at the Natural History Museum. The exact location of the samples in regard to the *in situ* deposit is unknown. They are Pragian (Early Devonian) in age based on palynology with an Ar/Ar radiometric age of 396 ± 12 Ma (Rice *et al.*, 1995). The main sample is $\sim 20 \times 30$ cm in size from which 2–5 cm blocks (*e.g.*, Fig. 1c) were removed with a water-based diamond saw. Three fresh pieces were cut and kept in a sterile desiccation jar to minimize contamination, and latex gloves and lab coats were worn to minimize human contamination during handling. After initial analyses, the samples were then made into polished thin sections and embedded in resin to create polished blocks. Two more blocks were crushed and further ground with an agate pestle and mortar to produce five $1\text{ g} < 25\text{ }\mu\text{m}$ sized powders. Analyses were performed throughout the samples to test areas that contained the cores of plant stems, plant cells, matrix materials, and structures that, during optical studies, resembled microorganisms previously documented. Seventy-five FTIR spot analyses were carried out on the samples, such that samples derived from all four preparation techniques—fresh surfaces, powdered samples, polished blocks, and polished thin sections—were included. Five powdered samples were run through the gas chromatograph–mass spectrometer (GCMS) to assure that both plant material and matrix material were analyzed. We were unable to produce more powdered samples due to the destructive nature of the technique and the need for preservation of the samples.

The mineralogy and biota of the chert samples were determined by optical microscopy of uncovered, polished thin sections and polished blocks. The thin sections were produced to a thickness of $30\text{ }\mu\text{m}$, with deionized water and a cover slip placed on top to allow imaging via transmitted light at different depths within the chert. The polished blocks were imaged by reflected light microscopy.

Infrared spectroscopy was carried out with a Perkin Elmer Spectrum One spectrometer with a Perkin Elmer AutoIMAGE FT-IR microscope attached. Samples of chert powders, polished blocks, and thin sections were analyzed over a spectral range of $4000\text{--}700\text{ cm}^{-1}$ with an aperture of $50 \times 50\text{ }\mu\text{m}$. Illumination of the samples was between 35% and 47%. Standard reference materials of gold and quartz were used.

Infrared spectroscopy is applicable in mineralogical and biological studies as different minerals and organic functional groups create vibrations that produce unique spectra. Due to their regular crystal structures, minerals have a restricted range of vibrational frequencies that are often characteristic. Vibrational frequency varies with bond strength and bond distance, which is a complex function of crystal structure, molecular symmetry, and composition. The vibrations interact with light, absorb it, and the light energy at various frequencies can be measured producing a spectrum.

Organic functional groups (*i.e.*, atom groups bonded in particular ways) differ with regard to the strength of the

bonds and the mass of the atoms involved. O–H and C=O functional groups each contain atoms of different masses, and they absorb IR radiation at different positions in the spectrum. For biological spectroscopy, the important vibrations occur in the mid-IR region ($700\text{--}4000\text{ cm}^{-1}$ or wavelengths between 2.5 and $16\text{ }\mu\text{m}$), where most organic molecules show characteristic spectral features (Naumann *et al.*, 1991; Diem, 1993) owing to different functional groups.

Gas chromatography–mass spectrometry was also conducted on the samples to identify any organic compounds present. Five samples of Rhynie Chert were powdered, weighed to 1.0 g , and placed into a 100 mm test tube. A solvent mixture of $97/3\text{ v/v}$ of dichloromethane/methanol was added to approximately three-quarters of the test tube. The solutions were ultrasonically extracted in an ultrasonic bath for 25 min at 25°C . They were then placed into the centrifuge at 2500 rpm for 10 min , and the supernatant solvent was removed with a pipette into another 100 mm test tube. This extraction was repeated three times and then left to dry underneath aluminum foil. Once the solvent had evaporated, $500\text{ }\mu\text{l}$ of dichloromethane was added and briefly shaken to mix the solution thoroughly.

Compound detection of hydrocarbons was performed with an Agilent Technologies 6890 GC coupled to an Agilent Technologies 5973 quadrupole mass selective detector with use of ZB-5 fused-silica capillary column ($30\text{ m}\times 0.25\text{ mm}$ inner diameter coated with $0.25\text{ }\mu\text{m}$ cross-linked 5% diphenyl– 95% dimethyl siloxane as stationary phase) and helium as carrier gas. Each analysis contained 1.0 g of chert powder, and blanks were prepared of pure dichloromethane. The samples were autoinjected with a splitless injector at 280°C . The column was heated from 50°C to 300°C at $5^\circ\text{C}/\text{min}$ followed by an isothermal period of 10 min . The mass selective detector was operated in the electron impact mode at 70 eV , source temperature of 250°C , emission current of 1 mA , and multiple-ion detection with a mass range from 50 to 550 amu . Compound identifications are based on GC retention time and mass spectrometric fragmentation patterns, which were compared with published literature. The data obtained from the GCMS are not quantitative; the sole purpose for acquisition of the data was to support results obtained through FTIR rather than to assess the concentrations of molecular species within the samples. There are, therefore, no analytical errors to present, and the results should be approached with the view of identification not quantification.

3. Results

3.1. Petrology and biota for biomolecular study

Mineralogical and biological subjects were found throughout the Rhynie Chert samples studied, with particular sites chosen for FTIR analysis. Detailed descriptions and images of the chert matrices, plant structures and associated microorganisms, and other microbial components of the samples are provided in Table 1. Identification of plant structures and microorganisms during the course of this study were based on morphological comparisons to previous studies in published literature. Cells in Table 1 images d–h are collections of spores or unicells that belong to green, and possibly red, algae, which have not been previously

described in the Rhynie Chert. The red cells are spherical, $\sim 10\text{ }\mu\text{m}$ in diameter, are observed as single or multiple phases, and bear a striking resemblance to cells observed by Butterfield (2000) of a 1.2 Ga old filamentous bangiophyte from arctic Canada. Affinities of fossil algae remain uncertain, primarily because modern classifications of algae are based on biochemical and ultrastructural features that are rarely, or never, preserved in the fossil record (Edwards and Lyon, 1983). Positive interpretations are hindered by the variable preservation of cell contents, size, and simple morphologies.

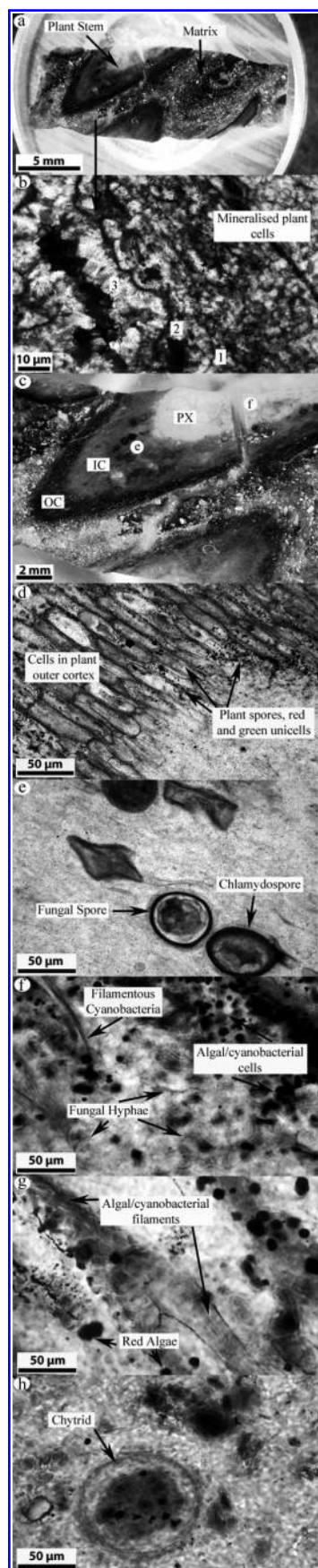
3.2. Infrared analysis

Infrared analyses were carried out on four varieties of Rhynie Chert media. The aim was, first, to identify any biomolecules present and, second, to assess which sample preparation type yielded the most informative mineralogical and biological results. The sample preparation that produced the better results would likely be the optimal method for future experiments and possible Mars sample return missions. Freshly cut smooth surfaces, powdered samples of $25\text{ }\mu\text{m}$ grain size, polished blocks, and polished thin sections were studied by using a $50\times 50\text{ }\mu\text{m}$ spot size. The freshly cut and powdered samples were used because they are analogous media to that which would be available on Mars for *in situ* analyses. The polished blocks and thin sections were used as they are standard practice in sample preparation and the best sample type for identification of silicified components within deposits. Further, their value in biomolecular studies needs to be evaluated.

3.2.1. Fresh surface. Analyses were conducted on a part of the fresh surface that included plant stems, layers of photosynthetic organisms, and the chert matrix, all of which were identified through reflected light microscopy. Spot analyses, shown in Fig. 2a, taken from the chert matrix, produced twin peaks at 1094 and 1204 cm^{-1} with a reflectance of 30% , recognized as quartz (*e.g.*, Wald and Salisbury, 1995) with no detectable bands indicative of organics. In the inner cortex of the plant stem, where degraded plant cells and spores are observed within the chert matrix (Fig. 2b), spectra show quartzlike peaks at 1090 and 1202 cm^{-1} and peaks representative of carboxyl group molecules, amides, and $\delta(\text{H}_2\text{O})$. The $\nu(\text{CH}_2)$ symmetric, $\nu(\text{CH}_2)$ asymmetric, and $\nu(\text{CH}_3)$ asymmetric bands occur at 2878 , 2950 , and 2976 cm^{-1} , respectively, and a broad $\nu(\text{OH})$ band occurs at around 3400 cm^{-1} . Finally, spectra were taken to encompass the better preserved plant cells with spore and cell-like bodies in the outer cortex of the stems (Fig. 2c). Spectra show a quartzlike response at 1080 and 1218 cm^{-1} . An uneven spectral signature exists up to 2000 cm^{-1} formed by functional groups such as amides, H_2O , C–C, CO, and COOH. The percentage reflectance of these is $<2.5\%$. At wavenumbers 2872 , 2958 , and 2974 cm^{-1} , $\nu(\text{CH}_2)$ symmetric, $\nu(\text{CH}_2)$ asymmetric, and $\nu(\text{CH}_3)$ asymmetric bands occur, respectively, and are connected to a broad $\nu(\text{OH})$ band from 3022 to 3594 cm^{-1} .

3.2.2. Thin sections. The thin sections were made from the fresh surfaces indicated above to allow for biomolecular comparisons of the same target areas. The thin sections

TABLE 1. REFLECTED AND TRANSMITTED LIGHT IMAGES PLUS DESCRIPTIONS OF AREAS AND SPECIFIC ORGANIC CONSTITUENTS THAT HAVE BEEN STUDIED AND USED FOR FTIR ANALYSES



The Rhynie Chert has a quartz (chert) matrix surrounding plant material which has replaced internal organic contents of plant cells, leaving the external cell walls unmineralised, either as left over organic material or pore spaces.

The samples have a fine grained inequigranular quartz matrix with a seriate and amygdular texture. Quartz crystals are anhedral, equant and commonly clear in colour showing undulose extinction effects owing to plastic deformation. Pores and fractures are observed that are lined with layers of quartz cement of different generations (layers 1, 2 and 3).

The plant stems are identified as *Aglaophyton major*, and fossilisation has outlined three areas: the outer cortex (OC), the inner cortex (IC) with loosely packed cells and severe degradation, and a centre of quartz that in life would have contained the phloem and xylem of the plant (PX). Within each of these areas are preserved micro-organisms that are shown in images d to h. Locations of images e and f shown.

The outer cortex of plant stems is composed of closely packed elongated cells of uniform size ($\sim 20 \mu\text{m}$ diameter). Evidence of plant spores, symbiotic and parasitic fungi, and algae are found within the outer cortex and at the boundary with the inner cortex.

Spores are identified of fungal affinities. They occur as individuals or as masses and range from $\sim 30 \mu\text{m}$ to $60 \mu\text{m}$. Several types of fungi produce resting spores, called Chlamydo spores, that are the life stage of the fungus and can survive unfavourable conditions. Spores in the samples appear intact, flattened, stretched or twisted.

Within the chert filled centre of the stems, brown radiating filaments of cyanobacteria (Krings *et al.*, 2007) are identified. The chert matrix has a clotted appearance due to endotrophic mycorrhizae, fungal hyphae that grow within cortical cells of plants sharing a symbiotic relationship (Taylor *et al.*, 1995). Individual cells are algal/cyanobacterial in origin.

Plant cells containing red/brown spores or unicells possibly of red algae not previously described within the Rhynie Chert. Green filaments ($3.5 \mu\text{m}$ diameter) are either cyanophytes (cyanobacteria) or chlorophytes (green algae) that contain chloroplasts. Cyanobacteria are seen to colonise plant axes through the outer cortical tissue (Taylor and Krings, 2005).

A Chytrid found within the chert matrix, outside of the plant stems. It is a parasitic fungus that contains eukaryotic algae and/or cyanobacteria. Chytrids are the most primitive of the fungi and are commonly found associated with freshwater systems.

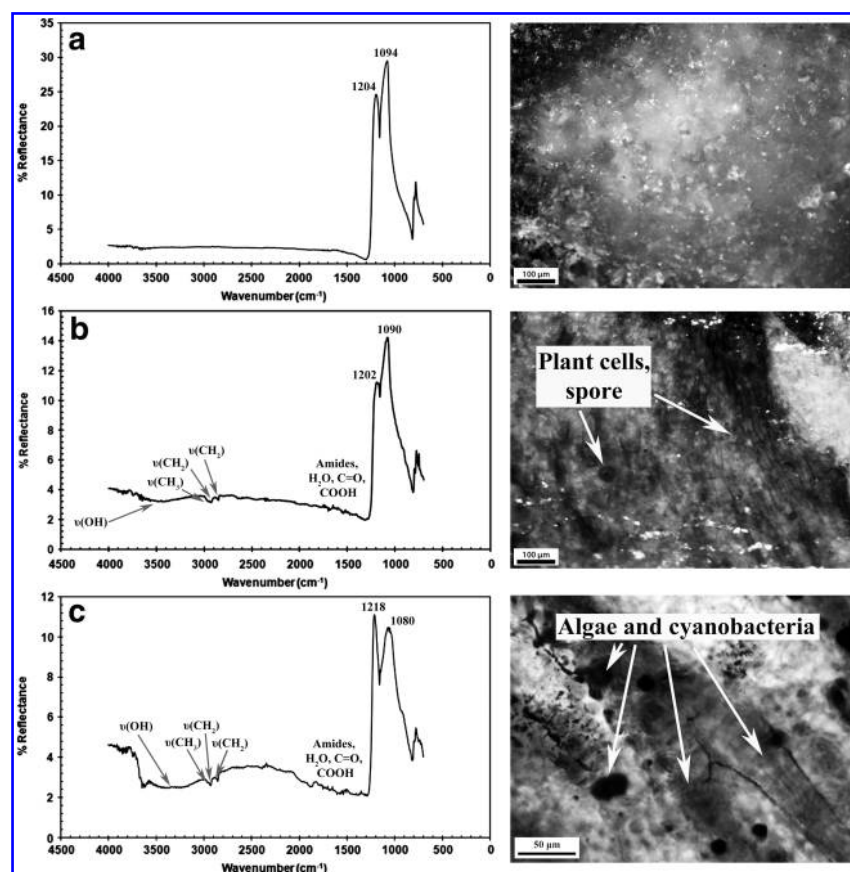


FIG. 2. (a) Reflected light image and representative IR spectrum of the chert matrix surrounding plant stems and filling voids. (b) Reflected light image and IR spectrum of an area within the inner cortex of Table 1c, where a spore and degraded plant cells are observed. (c) Transmitted light image and representative IR spectrum of plant cells in the outer cortex in Table 1g that contain evidence for algae or cyanobacteria, or both.

allowed for more detailed transmitted light microscopy identification of the types of organisms fossilized within the samples. Areas within and around plant stems, where spore and cell-like bodies were observed, were studied with FTIR reflected light; however, the expected organic reflectance bands were missing from all spectra (Fig. 3). Quartz (chert) spectra were recorded at all sites investigated, all of which resembled spectra of a pure chert matrix. This result is interesting, considering the known organic content of the selected areas.

3.2.3. Polished blocks. Due to the lack of organics observed within the thin sections, samples were made into polished blocks for further analysis. Initial results of all spectra taken throughout the plant axes where microorganisms had been observed previously show the twin peaks at 1100 and 1180 cm⁻¹ of chert with a relatively flat response at higher wavenumbers (Fig. 4). Closer examination, however, showed $\nu(\text{CH}_2)$ symmetric and $\nu(\text{CH}_2)$ asymmetric peaks at 2878 and 2942 cm⁻¹, respectively, but the common $\nu(\text{CH}_3)$ asymmetric band was absent. A broad $\nu(\text{OH})$ band occurs

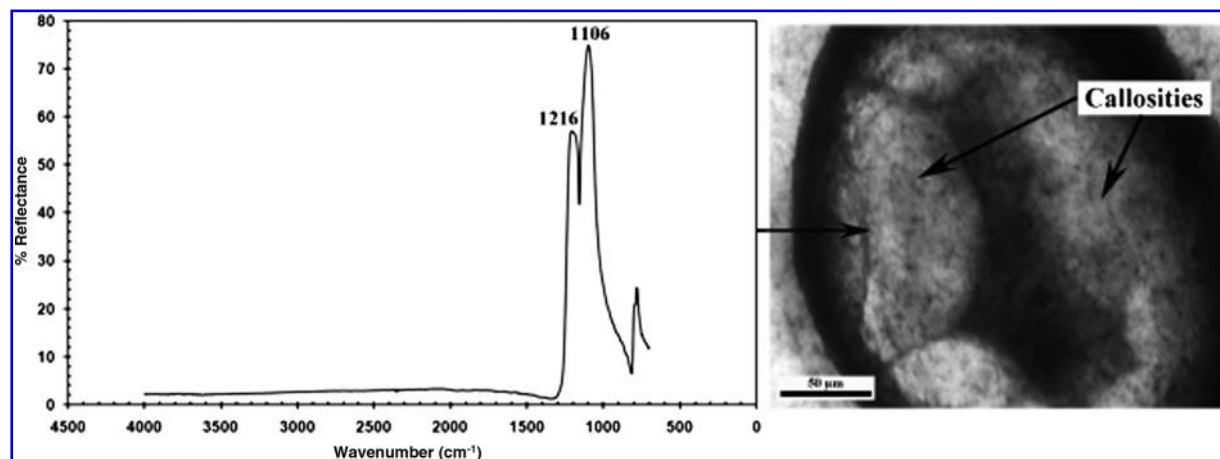


FIG. 3. Thin section transmitted light image and IR spectrum from inside a chlamydo spore seen in Table 1 image e. Callosities are thickened cell walls as a response to an invading mycoparasite (Godfrey, 1957).

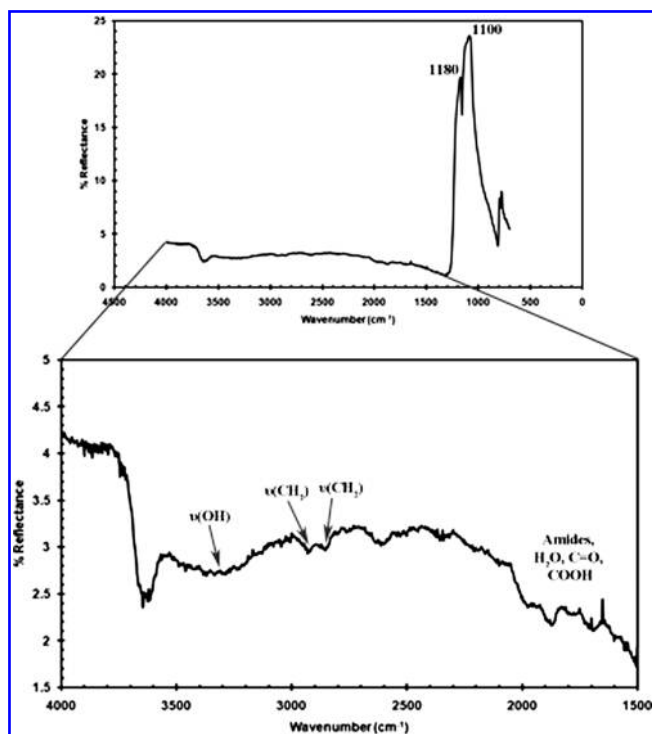


FIG. 4. Infrared spectra of a $50 \times 50 \mu\text{m}$ area known to contain evidence of algae/cyanobacteria. Spectra show minimal evidence for biomolecules in the magnified spectrum covering wavenumbers $1500\text{--}4000 \text{ cm}^{-1}$.

from 3172 to 3558 cm^{-1} as well as minor peaks that may have been caused by amides, $\delta(\text{H}_2\text{O})$, $\text{C}=\text{O}$, and COOH molecules between 1500 and 2000 cm^{-1} . The resin was analyzed, and no evidence of it was detected within the spectra taken from the samples.

3.2.4. Powdered samples. Average analyses of the powdered samples produced spectra such as that depicted in Fig. 5. The spectra show the twin peaks of quartz at 1082 and 1224 cm^{-1} but with a percentage reflectance of $<10\%$, 20% lower than the fresh chert matrix analyses. Peaks representative of carboxyl group molecules, amides, and $\delta(\text{H}_2\text{O})$ are observed. The $\nu(\text{CH}_2)$ symmetric, $\nu(\text{CH}_2)$ asymmetric, and $\nu(\text{CH}_3)$ asymmetric bands occur at 2882 , 2960 , and

2998 cm^{-1} , respectively, and a broad $\nu(\text{OH})$ band occurs around 3400 cm^{-1} .

3.3. Gas chromatography–mass spectrometry analysis

Gas chromatography–mass spectrometry was conducted on five powdered samples of the Rhynie Chert to help clarify the existence of the biomolecules observed via IR and to eliminate any effects of contamination. Multiple samples were tested to remove any sample heterogeneity; however, the same molecules were identified in each sample analyzed. In contrast to silica sinters studied by Preston *et al.* (2008), no fatty acid molecules were identified. Using a 57 mass-to-charge (m/z) extracted ion chromatogram, we show the alkanes present in the samples in Fig. 6. Alkanes with carbon numbers from $17\text{--}27$ were observed with no odd-number predominance. The pristine (Pr) and phytane (Ph) peaks have a medium ratio of 0.45 . Other high-abundance peaks are due to $1,2\text{-Benzenedicarboxylic acid}$.

4. Discussion

The Rhynie Chert represents one of the oldest silica sinters on Earth and therefore provides the opportunity of investigating the preservation of mineralogical, textural, and most importantly biochemical signatures of microorganisms within these siliceous deposits. FTIR reflectance spectroscopy has been shown by Preston *et al.* (2008) to be an effective technique with which to identify biomolecules within modern amorphous siliceous hydrothermal deposits. The Rhynie Chert provides the opportunity of investigating the degree of preservation of biomolecules over geological time.

In the Rhynie Chert analyses, the main mineral identified was microcrystalline quartz, which is visible in every spectrum obtained. The organic components of the chert are visible in reflected and transmitted light and can be seen within the spectra taken on fresh and powdered media. However, in polished block and thin section samples, the organic reflectance bands are minor to absent. Contamination is always a factor in studying organics within rocks. Particles from the air, human contact, and plastic containers during sample collection may have interacted with the specimens; however, the FTIR analyses only identified organic spectra in areas where the fossil evidence was observed. Pure chert matrices show no organics. The powdered

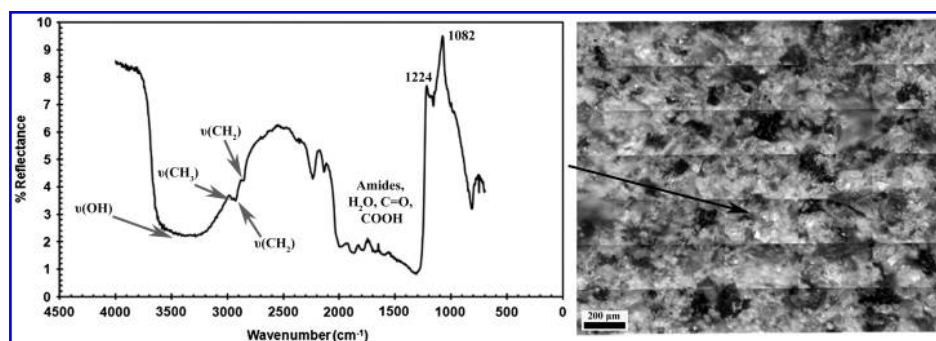


FIG. 5. Infrared spectrum and reflected light image from the powdered samples. Arrow indicates the location of the spectrum.

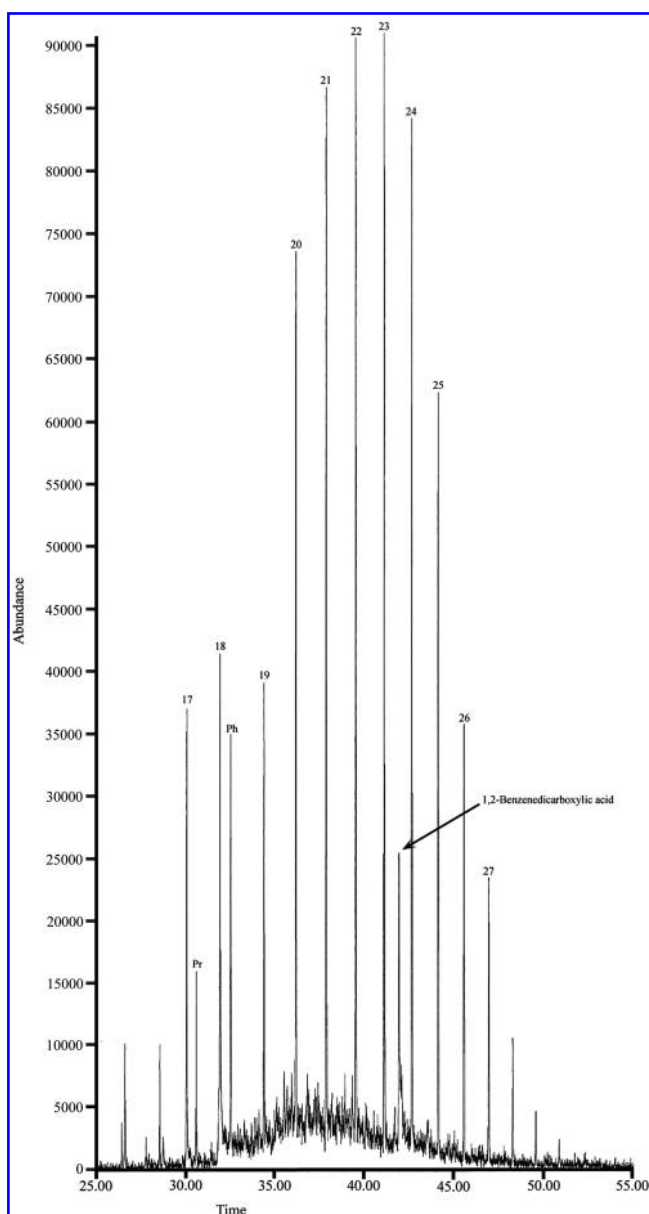


FIG. 6. 57 mass-to-charge (m/z) extracted ion chromatograph. Carbon numbers are placed above their respective alkane peaks. Ph, phytane; Pr, pristine.

sample may also have come into contact with airborne contaminants. With the addition of gas chromatography–mass spectrometry testing, we had hoped to confirm the existence of algal signatures within the samples. Standard contaminants found in gas chromatography–mass spectrometry–analyzed samples such as 1,2-Benzenedicarboxylic acid were observed. Before the samples were thin sectioned and placed into polished blocks, they and the equipment were washed in acetone to help minimize the amount of foreign particles that may have become trapped within them during preparation. The lack of organic spectra generated by fossil-rich sample areas in the thin section may be a result of polishing, which may have removed the top surfaces that contained more organic material. It may also be that the glass the sample was enclosed in attenuated the weaker organic IR

responses. The polished block shows minor organics, whose spectra may also have been affected by the media that enclosed the sample, though none of the media itself was identified in any spectra.

Within the IR spectra obtained, $\nu(\text{CH}_2)$ symmetric, $\nu(\text{CH}_2)$ asymmetric, and $\nu(\text{CH}_3)$ asymmetric bands can be indicative of fatty acids (Painter *et al.*, 1981), especially C^{16} and C^{18} . The carboxyl group molecules around 1600 cm^{-1} can be found within fatty acids but may have resulted from contamination. Peaks representing $\text{C}=\text{O}$ have been observed in lipid esters or as possible contributions from RNA/DNA (Yu and Irudayaraj, 2005), while amide bands can be found in proteins within microbial cells. FTIR in this study was used to identify the presence of molecular groups and organic compounds but could not necessarily provide a unique identification of the biomolecules or their concentrations. Further work will be carried out in this area. Hydroxyl is analyzed in the mid-IR due to broad O–H stretching vibrations at approximately 3490 cm^{-1} (Tamm and Tatulian, 1997), which may be an indication of fluid inclusions, water of hydration, or water held in a crystal structure (Anderson *et al.*, 2005). This band previously has been observed in chert and probably reflects H_2O present at grain boundaries of cryptocrystalline quartz (Nakashima *et al.*, 1995; Ito and Nakashima, 2002; Igisu *et al.*, 2006). Gas chromatography–mass spectrometry analysis identified alkanes, which are saturated hydrocarbons that can act as a scaffold for the addition of biologically active functional groups of a molecule. They can form fatty acids, which, when identified in geological samples and taken into consideration with other evidence, can be viewed as the degradation products of fatty acids and other biologically relevant molecules. The Rhynie Chert GCMS data contain a range of n -alkanes that may be suggestive of a contribution from the fossilized organisms since they support the observations of preserved unicells and filaments. Without other evidence, however, such as steroids to signal an algal input, these results are not conclusive. Although there is a high proportion of fossilized plant material in the samples, this is not evident in the analyses. The 1,2-Benzenedicarboxylic acids are part of a chemical group derived from phthalic acid, an organic compound that can form when hydrocarbons are oxidized by sulfuric acid. This biomolecule could have been formed due to the sulfuric environment of a hot spring postulated to have existed 396 Ma ago at Rhynie; however, contamination with plasticizers is also a possibility. The GCMS data are inconclusive, potentially because the solvent extractable organic matter is less abundant, as it represents only the small fraction that was originally soluble and persisted over time. It is not necessarily surprising, therefore, that the solvent extractable organic matter does not clearly, exactly match the organic material visible in thin section or that detected by FTIR. The latter two techniques are also spatially concentrated in certain areas, whereas the extracts represent mixtures that are more dispersed.

Research carried out by Boyce *et al.* (2001), who used electron microprobe carbon elemental mapping, showed that organic carbon in these fossilized plants and organisms in the Rhynie Chert is sporadic, with some cell walls constituting of up to 70% silica. This further hinders obtaining an FTIR hydrocarbon spectrum. Unlike hydrated opal-A ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) within modern silica sinters, the chert (SiO_2) in these samples does not contain appreciable water in the

crystal lattice; therefore, the broad $\nu(\text{OH})$ band observed may be caused by water contained within the sample in another form. Fluid inclusions within quartz grains have been observed (Rice *et al.*, 1995) and used together with fluorination of mineral and whole rock silicates to obtain $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and δD of the cherts and the fluids responsible for their formation. A low-salinity meteoritic fluid that interacted with basement rocks and sediments (Rice *et al.*, 1995) was responsible for the cherts, and this may be what is detected within the IR spectra. FTIR, optical microscopy, and gas chromatography–mass spectrometry techniques, although individually informative, are difficult to correlate to one another due to the irregular distribution of silica, carbon, and the fossilized material. Optical microscopy allowed fossil-rich areas to be imaged, and FTIR analysis indicated that they contain $\nu(\text{CH}_2)$ and $\nu(\text{CH}_3)$ plus carboxylic acids and amides. This correlation through individual spot analyses highlights the potential of these techniques for organic detection in other deposits; however, further research needs to be done before these organics can be characterized in more detail and correlated to their origins.

5. Relevance to Astrobiology

Knowledge of ancient terrestrial hydrothermal systems—how they preserve biological information and how this information can be detected—is important in unraveling the history of life on Earth and, perhaps, that of extinct life on Mars. On Earth, sites of hydrothermal activity support varied ecosystems in the surface and subsurface, and hydrothermal processes may have been of crucial importance in the development of early life on Earth (Stetter, 1996; Glasby, 1998; Reysenbach and Shock, 2002). Regions and features that exhibit evidence of this hydrothermal activity, therefore, should be targeted in the search for evidence of an extra-terrestrial fossil record (Farmer, 1998).

Some of the earliest morphological microfossils have been preserved by silicification, as seen in the 3490 Ma Dressler Formation (Van Kranendonk, 2006), the 3465 Ma Apex Chert (Schopf, 1993), and the 1.8 Ga Gunflint Chert (Barghoorn and Tyler, 1965), which demonstrates that silica precipitation is the most important process in the preservation of microorganisms over geologically significant periods. Silica ions in solution chelate to various exposed functional groups on the organic substrate, polymerize, and dehydrate, which replaces the original organic material (Westall *et al.*, 1995; Toppo, 2001) with organic molecules that remain trapped in the mineral matrix in varying degrees (Westall, 1999). Silicification preserves microorganisms and biomolecules via protection from later solutions and organic degradation. The resulting deposits are harder units and are therefore less prone to reworking and removal prior to burial. This type of preservation, as observed in the Rhynie Chert, is proven to maintain geochemical information for billions of years.

On Mars, rocks with coatings of amorphous silica have been identified via thermal IR spectroscopy (Kraft *et al.*, 2003; Michalski *et al.*, 2005), as has opaline silica in sedimentary rocks at Meridiani Planum (Glotch *et al.*, 2006) and within the Eastern Valley of Gusev Crater (Squyres *et al.*, 2008). These are an indicator of past aqueous activity, and one interpretation is that they formed under hydrothermal conditions (Squyres *et al.*, 2008) and may be akin to terrestrial silica

sinters formed by emissions of hot springs, such as the Rhynie Chert. Although deposits such as these, at present, are too small to be spectrally studied from orbit, *in situ* mid-IR analyses may provide biomolecular evidence of any past microbial residents. This study has shown that these signatures of life can still be detectable with FTIR nearly 400 million years after they formed. Compact Reconnaissance Imaging Spectrometer for Mars (Murchie *et al.*, 2007) observations of other regions on Mars suggest that there may be more widespread silica deposits around the planet, which highlights the growing possibility of discovering biological materials. These silica-rich deposits on Mars are strong candidates for examination by future rovers and for sample return missions. The results of this study are part of the groundwork for such a mission, though we emphasize that advances are needed in terms of sample preparation techniques for detailed astrobiological investigations.

6. Conclusions

The Rhynie Chert was originally deposited as sinter from Early Devonian hot springs and contains exceptionally well-preserved fossils of some of the earliest plants and animals to colonize the land. Plant stems of *Aglaophyton major* have been observed partially silicified with fungal chlamydospores and hyphae, plant spores, algal unicells, cyanobacteria, and a chytrid. FTIR analyses of the samples showed that studies conducted on broken, freshly exposed surfaces and powdered substrates yielded the most informative biomolecular information. Bands that represent $\nu(\text{CH}_2)$ symmetric and asymmetric and $\nu(\text{CH}_3)$ asymmetric bands connected to a broad $\nu(\text{OH})$ band are detected from areas containing algae, spores, and cyanobacteria. Analyses of the chert matrix produce quartz spectra (*e.g.*, Wald and Salisbury, 1995) with no detectable bands indicative of organics. The ability of FTIR to detect biomolecules within fresh and powdered surfaces akin to those found on Mars increases the potential for these organics to be identified within martian materials.

Silicified microfossils are more resistant to weathering or dissolution, which renders them more readily preservable over geological time. This is of particular interest in astro-paleontological research, considering the similarities of the early evolution of Mars and Earth. Microorganisms have been shown to be preserved in early Archean hydrothermal environments (*e.g.*, Westall and Walsh, 2000), and such environments may have been present on early Mars (Walter and Des Marais, 1993; Farmer, 1996). If life occurred at some point in Mars' history, microfossils would likely have been silicified by martian hot spring deposits such that they would be identifiable with IR spectroscopy.

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Abbreviations

FTIR, Fourier transform infrared; GCMS, gas chromatograph-mass spectrometer.

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